

NEW MATERIALS FOR ELECTROCHEMICAL CELLS(U) OXFORD UNIV
(ENGLAND) INORGANIC CHEMISTRY LAB

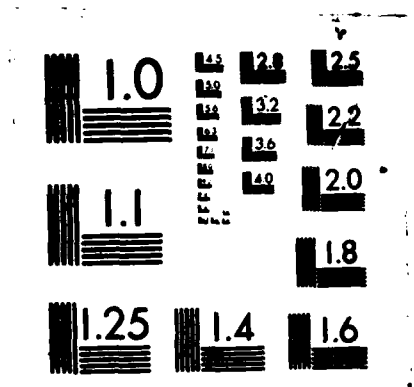
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<p>Thermochemical, structural and basic electrochemical properties have been determined for the hydrogen insertion compounds of V_2O_5, V_6O_{13}, VO_2, $Mo_yW_{1-y}O_3$, ReO_3 and for both hydrogen and lithium insertion into the uranium oxides U_3O_8, α-, γ- and δ-UO_3.</p> <p>The lithium insertion and extraction reactions of ternary oxides $Li[M_2]O_4$ with the spinel framework have been studied for $M = V, Mn, Fe, Ti$. Attempts to design new lithium cell cathode materials have centred on the thiospinels $Li_{1-x}[M_2]S_4$ where $M = Zr$ and Ti.</p>			
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9. PATENTS

No patents were applied for under this grant.

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research had two main aims: (i) determination of the thermochemical, structural and electrochemical properties of insertion compounds and materials showing mixed electronic/ionic conduction, and (ii) the design, preparation and characterisation of new materials for use as electrolytes or cathode materials in solid state cells. The progress of this research has been described in the series of scientific reports and renewal proposals submitted during the research period and discussed in detail through the scientific publications listed above.

New ambient-temperature lithium and hydrogen insertion compounds have been prepared from the uranium oxides U_3O_8 , UO_2 , and UO_3 . Electrochemical and thermochemical parameters have been determined for these phases and also for the hydrogen insertion compounds of V_2O_5 , V_6O_{13} , VO_2 , the mixed molybdenum-tungsten trioxides ($\text{Mo}_y\text{W}_{1-y}\text{O}_3$) and new structural modifications of WO_3 and MoO_3 ; the phase previously known as "hexagonal MoO_3 " has been shown to be a partially deammoniated and dehydrated ammonium decamolybdate. Where necessary this work has been accompanied by structural studies to locate the preferred insertion sites, and our understanding of the principles of

hydrogen and ammonium insertion into oxide lattices has been summarised in two recent conference papers.

The dynamics of mobile inserted species is another area of research which is central to the evaluation of materials for electrochemical-cell applications. The techniques of a.c.-conductivity and solid-state pulse nmr have been applied to the characterisation of lithium-ion motion in the battery cathode materials $\text{Li}_{1-x}\text{CoO}_2$ and Li_xMoO_3 , and proton motion in the polymer electrolyte Nafion, in electrochromic materials (H_xWO_3) and other materials of potential interest as solid-state proton conductors (phosphotungstic acid, $\text{HTa}(\text{Nb})\text{O}_3$, $(\text{H}_2\text{O})_x\text{H}_2\text{Ta}_2\text{O}_6$).

The design of new cathode materials has centred on materials with the spinel framework. Studies on the lithium insertion and extraction reactions of manganese oxo-spinels have proved of both scientific and technological significance, demonstrating the relationship between the $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ system and the " γ - MnO_2 " of a partially discharged $\text{Li}/\gamma\text{-MnO}_2$ dry cell.

Low-temperature preparations of the spinels $\text{Li}[\text{V}_2]\text{O}_4$ and $\text{Li}[\text{Ni}_2]\text{O}_4$ have been demonstrated, via lithium extraction from the layered oxides LiVO_2 and LiNiO_2 . The layered oxides LiVO_2 and LiCoO_2 have already been established as potentially valuable cathode materials.

Although the 3-D network of interstitial sites in the spinel framework permits diffusion of lithium ions, the room-temperature Li^+ ion mobility in an oxo-spinel framework is only adequate for low-power applications. In general, lithium-ion mobilities are higher in sulphide lattices. Therefore much attention has been paid to the thio-spinel framework. Lithium thio-spinels have been successfully prepared by the extraction and replacement of copper ions in $\text{Cu}[\text{Zr}_2]\text{S}_4$ and $\text{Cu}[\text{Ti}_2]\text{S}_4$.

A study of the low-temperature molten-salt system Aluminium Chloride-1-Methyl-3-ethylimidazolium Chloride has revealed that a maximum LiCl solubility of 12 mole-per-cent occurs in the room-temperature melt containing 0.62 mole-fraction of AlCl_3 . This composition has been shown to be stable against the thiospinel $\text{Li}_x\text{Cu}_{0.1}[\text{Ti}_2]\text{S}_4$ and the layered oxide $\text{Li}_{1-x}\text{CoO}_2$. A working cell with these two electrodes is calculated to give an open circuit voltage of about 1.8V, and such a cell was being constructed at the close of the contract period.

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